

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 1 104 806 A1**

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

(43) Date of publication:  
**06.06.2001 Bulletin 2001/23**

(21) Application number: **00935650.2**

(22) Date of filing: **13.06.2000**

(51) Int Cl.7: **C11D 17/06**

(86) International application number:  
**PCT/JP00/03813**

(87) International publication number:  
**WO 00/77158 (21.12.2000 Gazette 2000/51)**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**

(30) Priority: **14.06.1999 JP 16713999**

(71) Applicant: **Kao Corporation**  
**Tokyo 103-8210 (JP)**

(72) Inventors:  
• **SUGIYAMA, Yoichi, Kao Corporation**  
**Wakayama-shi, Wakayama 640-8580 (JP)**  
• **KITAGAITO, Hiroshi, Kao Corporation**  
**Wakayama-shi, Wakayama 640-8580 (JP)**

• **TAKANA, Shuji, Kao Corporation**  
**Wakayama-shi, Wakayama 640-8530 (JP)**  
• **TAKAYA, Hitoshi, Kao Corporation**  
**Wakayama-shi, Wakayama 640-8580 (JP)**  
• **YAMAGUCHI, Shu, Kao Corporation**  
**Wakayama-shi, Wakayama 640-8580 (JP)**  
• **YAMASHITA, Hiroyuki, Kao Corporation**  
**Wakayama-shi, Wakayama 640-8580 (JP)**

(74) Representative: **HOFFMANN - EITLÉ**  
**Patent- und Rechtsanwälte**  
**Arabellastrasse 4**  
**81925 München (DE)**

**(54) GRANULAR BASE AND PARTICULATE DETERGENT**

(57) The present invention relates to a preparation of a high-bulk density detergent. Concretely, it provides base particles for supporting a surfactant, obtainable by spray-drying a slurry comprising a water-soluble polymer (A), an inhibitor for forming a coating film (B) and a water-soluble salt (C) other than the inhibitor for forming a coating film, wherein the surfactant is contained in an amount of from 0 to 10% by weight of the base particles; a process for preparing the base particles; detergent particles having an average particle size of from 150 to 750 µm and a bulk density of 500 g/L or more, wherein

1 to 100 parts by weight of a surfactant is supported in 100 parts by weight of the base particles; and a detergent composition comprising the detergent particles.

Since the base particles for supporting a surfactant and the detergent particles of the present invention have excellent dissolubility and sufficient bulk density, and further have extremely high oil-absorbing ability, there are exhibited effects so that there can be obtained a detergent composition in which the dissolubility is excellent and the caking property and the bleed-out property are suppressed.

**EP 1 104 806 A1**

**Description**TECHNICAL FIELD

- 5 [0001] The present invention relates to base particles for supporting a surfactant (hereinafter referred to as "base particles"), and detergent particles.

BACKGROUND ART

- 10 [0002] In high bulk-densifying of the powdery detergent in the latter half of 1980's, its compactness has greatly contributed to transportation or hand-carry and housability. Therefore, compact detergents are the mainstream at present.

- [0003] A number of studies have been made on processes for preparing a high-bulk density detergent, one of which is a technique comprising supporting a surfactant to base particles obtained by spray-drying. This technique has merits in that a nonionic surfactant which is excellent in the detergency for sebum dirt stains and is in a liquid state at a normal temperature can be formulated in a large amount.

- [0004] However, in a base particle having low oil-absorbing ability, there is a concern about bleed-out of a surfactant, or the like when a surfactant is absorbed in an amount sufficient for satisfying the detergency. Also, it is not preferable to use a large amount of a surface-modifying agent for suppressing bleed-out from the economic viewpoint. Therefore, in order to make use of this technique, it is necessary that the oil-absorbing ability of the base particles is at an extremely high level. As techniques for improving an oil-absorbing ability of the base particles, Japanese Patent Laid-Open Nos. Sho 57-159898 and Sho 60-262898 each discloses a technique for improving an oil-absorbing ability comprising decomposing a part of sodium bicarbonate existing in crutcher mix during spray-drying to release carbon dioxide, thereby expanding the base particle. However, in this technique, since the base particle is expanded, there arise problems such that the bulk density is lowered, and that since sodium bicarbonate remains in the detergent, an alkali buffer range (pH value) of sodium carbonate or sodium silicate usable as an alkalizing agent is lowered, thereby lowering the detergency against sebum dirt stains.

- [0005] Accordingly, an object of the present invention is to provide base particles having a sufficiently large bulk density for use in compact detergents, and further very large oil-absorbing ability; and detergent particles comprising uni-core detergent particles comprising base particles and a surfactant supported thereto.

- [0006] These and other objects of the present invention will be apparent from the following description.

DISCLOSURE OF INVENTION

- 35 [0007] Specifically, the gist of the present invention relates to:

[1] base particles for supporting a surfactant, obtainable by spray-drying a slurry comprising a water-soluble polymer (A), an inhibitor for forming a coating film (B) and a water-soluble salt (C) other than the inhibitor for forming a coating film, wherein the surfactant is contained in an amount of from 0 to 10% by weight of the base particles;

- 40 [2] base particles for supporting a surfactant, obtainable by spray-drying a slurry comprising at least a water-soluble polymer (A) and an alkali metal halide, wherein the surfactant is contained in an amount of from 0 to 10% by weight of the base particles, and wherein a weight ratio of the water-soluble polymer to the alkali metal halide in a base particle constituting the base particles, i.e. water-soluble polymer/alkali metal halide, is from 0.1 to 100;

- 45 [3] a process for preparing base particles for supporting a surfactant, the base particles containing the surfactant in an amount of from 0 to 10% by weight, comprising the step of spray-drying a slurry comprising a water-soluble polymer (A), an inhibitor for forming a coating film (B) and a water-soluble salt (C) other than the inhibitor for forming a coating film, wherein a dissolution ratio of Component (B) in the slurry is at a level sufficient to inhibit formation of a coating film on the surface of the resulting base particles; and

- 50 [4] detergent particles having an average particle size of from 150 to 750  $\mu\text{m}$  and a bulk density of 500 g/L or more, wherein 1 to 100 parts by weight of a surfactant is supported by 100 parts by weight of the base particles of items [1] or [2] above.

BEST MODE FOR CARRYING OUT THE INVENTION

- 55 1. Base Particles

[0008] Base particles obtained by spray-drying a slurry, a paste or an aqueous solution (hereinafter referred to as a slurry in the present invention) having a low surfactant content, the base particles substantially comprising detergent

builder components such as a water-soluble polymer, a water-soluble salt and a water-insoluble inorganic compound, have only exhibited an extremely low oil-absorbing ability, as compared to an oil-absorbing ability (expected value) estimated from a specific surface area of a base material or a microporous capacity of a base particle. Therefore, the present inventors have studied on the causes therefor, and have elucidated that a water-soluble polymer component, which is a component for securing the particle strength of a base particle, tends to be localized on the surface of the base particle and in the vicinity thereof during a spray-drying process, and as a result, an amorphous coating film comprising a water-soluble polymer and a water soluble-salt, is formed on the surface of the base particle. Based on this finding, the present inventors have considered that the base particle has a surface condition inappropriate for supporting and/or oil-absorbing a surfactant which is an oily substance, so that the base particle could not fully exhibit the inherently owned oil-absorbing ability. The present inventors have further studied on the spray-drying process and the base particle, and as a result, they have found that a certain kind of substance has an inhibitory ability for forming a coating film, and that when this substance is contained in the slurry, a coating film is not formed on the surface of the base particle obtained by spray-drying, or if formed, the thickness thereof is thin, whereby consequently the surface condition of the resulting base particle can be made into a state in which a surfactant can be easily supported and oil-absorbed.

**[0009]** The base particles of the present invention are an aggregate of base particle, of which a surfactant content is from 0 to 10% by weight. Here, in the case where the base particle is prepared by spray-drying a slurry comprising a surfactant, since a coating film tends to be formed on the surface of the resulting base particle, and consequently the oil-absorbing ability of the base particles can be lowered. Therefore, from this viewpoint, the smaller the content of the surfactant in the base particles, the more preferable, and it is most preferable that the base particles comprise substantially no surfactant.

**[0010]** On the other hand, there is an advantage that the drying efficiency during spray-drying is improved by adding a surfactant to the slurry. Therefore, from this viewpoint, it is preferable that a surfactant is formulated in the base particles. From the above viewpoints, the content of the surfactant in the base particles is more preferably from 0 to 5% by weight, especially preferably from 0 to 3% by weight.

**[0011]** Examples of the surfactant used herein include a surfactant supported in base particles.

**[0012]** The bulk density of the base particles of the present invention is preferably from 400 to 1000 g/L, more preferably from 450 to 800 g/L, most preferably from 500 to 650 g/L, in order to support a surfactant with maintaining the uni-core property of the base particle, and to have a bulk density necessary for a compact detergent. In addition, the average particle size of the base particles is preferably from 150 to 500  $\mu\text{m}$ , more preferably from 180 to 300  $\mu\text{m}$ . In addition, the base particles can support a large amount of a nonionic surfactant having a melting point of 40°C or lower which is effective for sebum dirt stains in a low-temperature range. The oil-absorbing ability of the base particles described above, as determined by a nonionic surfactant dropping method as described below, is preferably 0.25 g/g or more, more preferably 0.30 g/g or more, still more preferably 0.35 g/g or more, most preferably 0.40 g/g or more.

**[0013]** In the base particles of the present invention, from the viewpoint of easy support and oil-absorption of a surfactant, it is preferable that an inhibitor for forming a coating film is present on the surface of the base particle and/or in the vicinity thereof. Whether or not an inhibitor for forming a coating film is present on the surface of the base particle and/or in the vicinity thereof can be found by analyzing the base particles by a scanning electron microscope (SEM) observation, energy dispersion-type X-ray spectroscopy (EDS) or the like.

**[0014]** In the base particles of the present invention, in order to further enhance the inhibitory effect of forming a coating film in the base particle, it is preferable that the inhibitor for forming a coating film is present in the base particle as crystals.

**[0015]** The phrase "inhibitor for forming a coating film is present ... as crystals" means that a peak ascribed to an inhibitor for forming a coating film is detected when a powder method of X-ray diffraction analysis for the base particles is carried out. Sodium carbonate, sodium sulfate and the like, which are generally used as a water-soluble salt formulated in a detergent, are easily compatible with a water-soluble polymer, and tend to partly become amorphous. On the other hand, since an alkali metal halide tends to be crystallized, the alkali metal halide is crystallized alone, and usually is present as crystals in the base particle in the present invention. From this viewpoint, it is also preferable that an alkali metal halide is used as an inhibitor for forming a coating film.

#### Component (A)

**[0016]** The water-soluble polymer of Component (A) is an organic polymer having a solubility of 0.5 g or more in 100 g of water at 25°C and a molecular weight of 1000 or more. The water-soluble polymer is not particularly limited, as long as it has an effect of improving the detergency and/or improving the particle strength of the base particle. The preferred water-soluble polymer can be exemplified, for instance, one or more kinds selected from the group consisting of carboxylic acid-based polymers; cellulose derivatives such as carboxymethyl cellulose; aminocarboxylic acid-based polymers such as polyglyoxylates and polyaspartates; soluble starches; sugars; and the like. Among them, the car-

boxylic acid-based polymers are more preferable.

[0017] Among the carboxylic acid-based polymers, the salts (Na, K,  $\text{NH}_4$ , and the like) of acrylic acid-maleic acid copolymers and the salts (Na, K,  $\text{NH}_4$ , and the like) of polyacrylic acids are especially excellent. Above all, those having a molecular weight of 1000 to 100000 are preferable, those having a molecular weight of 2000 to 80000 are more preferable, and those having a molecular weight of 5000 to 50000 are most preferable.

[0018] The content of the water-soluble polymer is preferably from 2 to 20% by weight, more preferably from 3 to 17% by weight, most preferably from 4 to 12% by weight, in the base particles. When the content is within the above range, the base particle has a sufficiently high particle strength, and the dissolubility of the detergent composition also becomes excellent.

#### Component (B)

[0019] The inhibitor for forming a coating film of Component (B) is a substance which is added to a slurry comprising a water-soluble polymer (A), a water-soluble salt (C) other than the inhibitor for forming a coating film and, as occasion demands, a water-insoluble inorganic compound (D), to have a function of shortening a drying time for the slurry (also referred to as a drying accelerator). Here, the water-soluble salt refers to those having a solubility of 0.5 g or more in 100 g of water at 25°C and a molecular weight of less than 1000. The water-insoluble compound refers to those having a solubility of less than 0.5 g in 100 g of water at 25°C. In addition, the inhibitor for forming a coating film is a substance which has a function of making the surface of the dried particle roughened or discontinuous when contained in the slurry, and make the surface condition of the base particle into a state of easy support and/or oil-absorption of a surfactant. The inhibitor for forming a coating film can be confirmed by the fact that a time required for drying (drying time) is shortened as compared to a case where the inhibitor for forming a coating film is not contained, when subjecting a slurry comprising Component (A), Component (C) and, as occasion demands, Component (D) to thin-film drying with a far infrared ray moisture balance (for instance, one manufactured by SHIMADZU CORPORATION, Model: EB-340MOC), a drying method comprising evenly placing 3 g of a slurry on a sample plate and heating the slurry to make a slurry water content of 50% by weight to 3% by weight, to form a thin film. In addition, when drying, the longer the constant drying rate period and the shorter the falling drying rate period, the more preferable. Further, when the thin film formed is observed by SEM, the rougher the surface of the thin film or the more discontinuous, the more preferable.

[0020] The inhibitor for forming a coating film includes, for instance, one or more kinds selected from the group consisting of halides of alkali metals and alkaline earth metals such as chlorides, bromides, iodides or fluorides of sodium, potassium, calcium, magnesium, and the like. The chlorides are preferable, from the viewpoints of the storage stability of the detergent particles, and the like, and the alkali metal salts are preferable from the viewpoint of the effect on the detergency. Among them, sodium chloride is especially preferable from the economical viewpoint.

[0021] In the case where the halide is used as an inhibitor for forming a coating film, the inhibitor for forming a coating film may be finally present as a halide in the base particle, and the process for formation or the process for addition are not limited. It is especially preferable to formulate a corresponding halide *per se* in a slurry. As an alternative method, a halogen-containing compound such as hydrochloric acid may be formulated in a slurry to carry out the reaction such as salt-interchanging reaction in the slurry, thereby finally forming the desired halogen-containing compound in the base particle. In this case, there are included, for instance, a combination of hydrochloric acid and sodium hydroxide, and a combination of hydrochloric acid and sodium carbonate.

[0022] The content of the inhibitor for forming a coating film is preferably from 0.2 to 20% by weight, more preferably from 1 to 12% by weight, especially preferably from 2 to 8% by weight, in the base particles, from the viewpoints of a sufficient inhibitory effect of forming a coating film and the detergency.

[0023] The weight ratio of the water-soluble polymer to the inhibitor for forming a coating film in the base particle constituting the base particles, i.e. a water-soluble polymer/inhibitor for forming a coating film, is preferably from 0.1 to 100, more preferably from 0.3 to 12, especially preferably from 0.6 to 4.5, most preferably from 1 to 2.5. When the weight ratio in the base particle is 100 or less, it is preferable because a coating film forming on the surface of the base particle can be inhibited, whereby accomplishing improvement in the oil-absorbing ability of the base particles. In addition, when the weight ratio is 0.1 or more, it is preferable because the particle strength of the base particle can be sufficiently secured.

#### Component (C)

[0024] The water-soluble salt excluding the inhibitor for forming a coating film, which is Component (C), includes, for instance, water-soluble inorganic salts such as alkali metal salts, ammonium salts or amine salts having carbonate group, hydrogencarbonate group, sulfate group, sulfite group, hydrogensulfate group, or phosphate group; and water-soluble organic acid salts having low-molecular weights such as citrates and fumarates. Among them, salts having carbonate group, sulfate group, and sulfite group are preferable. Component (C) may be constituted by a singular

component, or by plural components.

**[0025]** Here, sodium carbonate is preferable as an alkalizing agent showing a suitable pH buffer region in the washing liquid. In addition, the salts having a high degree of dissociation such as sodium sulfate, potassium sulfate and sodium sulfite enhance ionic strength of the washing liquid, thereby favorably acting on deterging against sebum dirt stains, and the like. In addition, the sulfite group has an effect of reducing hypochlorite ions contained in tap water, thereby preventing oxidation degradation of the detergent components such as enzymes and perfumes by the hypochlorite ions. In addition, sodium tripolyphosphate can be used as Component (C).

**[0026]** The water-soluble organic acid salts having low-molecular weights include carboxylic acids such as citrates and fumarates, and those base materials having a large  $pKCa^{2+}$  and/or having a large cationic exchange capacity are preferable in expectation of imparting the metal ion capturing ability. Concretely, from the viewpoint of detergency, there can be also included as preferred ones methyliminodiacetates, iminodisuccinates, ethylenediaminedisuccinates, taurine diacetates, hydroxyethyliminodiacetates,  $\beta$ -alanine diacetate, hydroxyiminodisuccinates, methylglycine diacetate, glutamic acid diacetate, asparagine diacetate, serine diacetate, and the like.

**[0027]** In addition, when anions different from carbonate group, such as sulfate group and sulfite group, and cations different from sodium, such as potassium and ammonium, are mixed in the base particle, there is an effect for the anti-paste formability.

**[0028]** Incidentally, an amorphous silicate has an action of enhancing the particle strength of the particles for supports. However, in the case where the aluminosilicate is used as a water-insoluble compound to be contained in the base particles for supports, aggregated masses which become hardly soluble to water with the passage of time are formed when an amorphous silicate is formulated in a slurry for preparing base particles for supports, so that it is preferable that the base particles for supports of the present invention comprise substantially no amorphous silicate.

**[0029]** The content of the water-soluble salt is preferably from 5 to 75% by weight, more preferably from 10 to 70% by weight, most preferably from 20 to 60% by weight, in the base particles. When the content is within the above ranges, it is preferable because the base particle has sufficiently high particle strength, and the dissolubility of the detergent particles is excellent.

#### Component (D)

**[0030]** The water-insoluble inorganic compound of Component (D) is those having a primary average particle size of preferably from 0.1 to 20  $\mu m$ , more preferably from 0.5 to 10  $\mu m$ . The water-insoluble inorganic compound includes, for instance, crystalline aluminosilicates, amorphous aluminosilicates, silicon dioxide, hydrated silicate compounds, clay compounds such as perlite and bentonite, and the like. Crystalline aluminosilicates are preferable from the viewpoints of the detergency and not causing the occurrence of undissolved remnants of the detergent, and the like.

**[0031]** Those preferable as the crystalline aluminosilicates are A-type zeolites (for instance, trade name: "TOY-OBUILDER," manufactured by Tosoh Corporation), which are also preferable from the viewpoints of the metal ion capturing ability and the economic advantages. Here, it is preferable that the value for the oil-absorbing ability of A-type zeolite measured by a method according to JIS K 5101 is 40 to 50 mL/100 g. Besides the above, preferable crystalline aluminosilicates include P-type (examples include trade names: "Doucil A24" and "ZSE064", each manufactured by Crosfield B.V.; oil-absorbing ability: 60 to 150 mL/100 g); X-type (examples include trade name: "Wessalith XD"; manufactured by Degussa-AG; oil-absorbing ability: 80 to 100 mL/100 g), and hybrid zeolite described in WO 98/42622.

**[0032]** As the amorphous aluminosilicates, from the viewpoint of maintaining high dissolubility even after stored for a long period of time (without undergoing property changes), its molar ratio of  $SiO_2/Al_2O_3$  is preferably 5.0 or less, more preferably 4.0 or less, still more preferably 3.3 or less. The amorphous aluminosilicates include, for instance, those described in Japanese Patent Laid-Open No. Hei 6-179899, column 12, line 12 to column 13, line 1 and column 17, line 34 to column 19, line 17. Among them, those with a volume of 0 to 0.7 mL/g of pores having a pore size, as determined by a mercury porosimeter (manufactured by SHIMADZU CORPORATION, "SHIMADZU Poresizer 9320"), of 0.015 to 0.5  $\mu m$ , and with a volume of 0.30 mL/g or more of pores having a pore size of 0.5 to 2  $\mu m$ , are preferable. Component (D) may be constituted by a singular component, or by plural components.

**[0033]** The content of the water-insoluble inorganic compound is preferably from 20 to 90% by weight, more preferably from 20 to 75% by weight, most preferably from 25 to 70% by weight, in the base particles. When the content is within the above ranges, the base particle having an excellent particle strength and dissolubility can be obtained.

**[0034]** From the viewpoints of improvements in the detergency and the oil-absorbing site in the inner portion of the base particle, it is preferable that the base particles further comprise a water-insoluble inorganic compound (D).

**[0035]** In addition, the base particle may comprise components other than the above components, for instance, a surfactant, and auxiliary components suitable for a detergent composition, such as a fluorescent dye, a pigment and a dye. In addition, the water content is preferably from 1 to 10% by weight, more preferably from 1.5 to 8% by weight, still more preferably from 2 to 6% by weight, most preferably from 2 to 5% by weight, in the base particle, as determined

by an infrared moisture balance.

[0036] Specific embodiments of the base particles of the present invention is described below.

Embodiment [1] Base particles, obtainable by spray-drying a slurry comprising a water-soluble polymer (A), an inhibitor for forming a coating film (B) and a water-soluble salt (C) other than the inhibitor for forming a coating film, wherein the surfactant is contained in an amount of from 0 to 10% by weight of the base particles.

Embodiment [2]: Base particles, obtainable by spray-drying a slurry comprising at least a water-soluble polymer (A) and an alkali metal halide, wherein the surfactant is contained in an amount of from 0 to 10% by weight of the base particles, and wherein a weight ratio of the water-soluble polymer to the alkali metal halide of the base particle constituting the base particles, i.e. water-soluble polymer/alkali metal halide, is from 0.1 to 100.

[0037] The base particles of Embodiment [1] are an embodiment wherein the base particles are obtained from a slurry comprising each of Components (A) to (C), and the base particles of Embodiment [2] are an embodiment wherein the base particles are obtained from a slurry comprising at least Component (A) and an alkali metal halide, which is a preferred example of Component (B). The slurry in both Embodiments may further comprise Component (D).

## 2. Detergent Particles and Detergent Composition

[0038] The "detergent particle" as referred to in the present invention is preferably a particle comprising a surfactant, a builder and the like, and the "detergent particles" as referred to in the present invention is an aggregate thereof. Although the detergent particles of the present invention can take either an embodiment of uni-core detergent particles or an embodiment of multi-core detergent particles, the uni-core detergent particles are preferable. Here, in the detergent particles, 1 to 100 parts by weight of the surfactant is supported in 100 parts by weight of the base particles. The detergent particles have an average particle size of 150 to 750  $\mu\text{m}$  and a bulk density of 500 g/L or more.

[0039] As the surfactant, an anionic surfactant and a nonionic surfactant are preferable. The anionic surfactant and the nonionic surfactant can be used alone, or it is more preferable to use the anionic surfactant and the nonionic surfactant in admixture. In addition, an amphoteric surfactant or a cationic surfactant can be also used in combination therewith in accordance with its purpose. Also, when an anionic surfactant such as an alkylbenzenesulfonate is formulated in the detergent particles in an amount of 5 to 25% by weight, an effect is exhibited in the non-paste formability in water.

[0040] The average particle size of the detergent particles of the present invention is preferably from 150 to 750  $\mu\text{m}$ , more preferably from 200 to 450  $\mu\text{m}$ , especially preferably from 220 to 350  $\mu\text{m}$ , from the viewpoints of the dissolubility, the powder texture and the storage stability. In addition, its bulk density is preferably from 500 to 1200 g/L, more preferably from 600 to 900 g/L, especially preferably from 650 to 800 g/L, from the viewpoints of the transport and the housing ability, and the viewpoint of the dissolubility.

[0041] The detergent composition in the present invention is a composition comprising the above-mentioned detergent particles, and further comprising separately added detergent components other than the detergent particles (for instance, builder particle, fluorescent dye, enzyme, perfume, defoaming agent, bleaching agent, bleaching activator, and the like).

[0042] The content of the detergent particles is preferably 50% by weight or more, more preferably 60% by weight or more, still more preferably 70% by weight or more, especially preferably 80% by weight or more, in the detergent composition, from the viewpoint of the detergency.

## 3. Process for Preparing Base Particles

[0043] The base particles of the present invention can be obtained by a process comprising the step of spray-drying a slurry comprising a water-soluble polymer (A), an inhibitor for forming a coating film (B) and a water-soluble salt (C) other than the inhibitor for forming a coating film, wherein the dissolution ratio of Component (B) in the slurry is at a level sufficient to inhibit the formation of a coating film on the surface of the resulting base particles. Concrete examples of the process include a process comprising Steps (a) and (b) given below. Incidentally, the base particles of Embodiment [2] can also be prepared according to this process.

### <Step (a)>

[0044] Step (a) comprises preparing a slurry comprising given components. The resulting slurry preferably has a property that is liquid-conveyable with a pump and is non-curable.

[0045] The dissolution ratio of the inhibitor for forming a coating film is at a level sufficient to inhibit the formation of a coating film on the surface of the resulting base particles. For instance, in order that the particle of the base particles

obtained in Step (b) described below (drying step) has a preferable structure such that the inhibitor for forming a coating film is present on the surface and/or in the vicinity thereof, it is desired that the inhibitor for forming a coating film is migrated to the particle surface along with water evaporation during the drying step. For this purpose, the weight ratio of the water-soluble polymer in the slurry to the inhibitor for forming a coating film dissolved in the slurry, i.e. water-soluble polymer/inhibitor for forming a coating film, is preferably 100 or less, more preferably from 0.15 to 100, still more preferably from 0.3 to 12, especially preferably from 0.6 to 4.5, most preferably from 1 to 2.5. The weight ratio is preferably 100 or less, from the viewpoint of suppressing the formation of a coating film, and the weight ratio is preferably 0.15 or more, from the viewpoint of formulating a given amount or more of other components such as a surfactant and a builder. In addition, a slurry is prepared so that the dissolution ratio of the inhibitor for forming a coating film is preferably 60% by weight or more, more preferably 70% by weight or more, still more preferably 85% by weight or more, especially preferably 90% by weight or more. For this purpose, the water content in the slurry is preferably from 30 to 70% by weight, more preferably from 35 to 60% by weight, especially preferably from 40 to 55% by weight, most preferably from 45 to 55% by weight.

[0046] The dissolution ratio of the inhibitor for forming a coating film in the slurry can be determined by utilizing a combination of known analytic methods. For instance, a slurry is filtered under reduced pressure, and a water concentration P (%) in the filtrate is determined by a far infrared ray heating-type moisture balance (manufactured by SHIMADZU CORPORATION) and the like. Further, the concentration S (%) of the inhibitor for forming a coating film in the filtrate is obtained by ion chromatography or the like. Supposing that the water content of the slurry is Q (%) and that the content of the inhibitor for forming a coating film in the slurry is T (%), the dissolution ratio of the inhibitor for forming a coating film is obtained by the following equation:

$$\text{Dissolution Ratio (\%)} = \frac{S \times Q}{P \times T} \times 100$$

[0047] However, when the above dissolution ratio calculated exceeds 100%, the dissolution ratio is considered as 100%.

[0048] The amount of each component to be dissolved in the slurry can be appropriately set depending on the water content of the slurry, the order of addition of slurry components, the temperature of the slurry and the desired content of each component in the base particles.

[0049] The temperature of the slurry is preferably from 30° to 80°C, still more preferably from 35° to 75°C, from the viewpoints of the solubility of the water-soluble components (A, B and C) and the liquid conveyability thereof with a pump.

[0050] As a process for preparing a slurry, the process and the order of addition of the components can be appropriately modified depending upon the conditions. For instance, all or substantially all of water are initially added to a mixing vessel, and other components are sequentially or simultaneously added thereto, preferably after the water temperature almost reaches a set temperature, preferably a temperature of 30° to 45°C. A usual order of addition is such that liquid components are initially added, and thereafter water-soluble, powdery raw materials are added thereto. In addition, small amounts of auxiliary components such as dyes are also added. Finally, the water-insoluble components are added. At this time, the water-insoluble components may be added in two or more divided portions, for the purpose of improving the mixing efficiency. In addition, powdery raw materials are previously mixed, and the mixture may be added to an aqueous medium.

[0051] The inhibitor for forming a coating film may be added initially or finally, or added in divided portions, so long as the dissolution ratio is retained at a level sufficient to inhibit the formation of a coating film. Here, in the case where sodium sulfate and sodium carbonate are formulated as Component (C) to use sodium chloride as an inhibitor for forming a coating film, it is preferable that sodium sulfate, sodium carbonate and sodium chloride are added in this order, because the oil-absorbing ability of the base particles can be further improved. This is because sodium chloride is dissolved in a saturated solution of sodium sulfate and sodium carbonate, whereby fine crystals of burkeite, which is a double salt of sodium sulfate and sodium carbonate, are precipitated, and consequently there is exhibited an effect of increasing oil-absorbing sites in the inner portion of the base particle. In addition, in the case where sodium chloride is used, sodium chloride is not necessarily added at all as sodium chloride, and a compound which dissolves in a slurry to elute chloride ions and sodium ions, for instance, a combination of hydrochloric acid and sodium hydroxide, and a combination of hydrochloric acid and sodium carbonate, or the like may be added. This is because when sufficient chloride ions and sodium ions are present in the slurry, sodium chloride is precipitated on the surface as crystals during the drying step. In order to finally obtain a homogeneous slurry, after the addition of the entire components to the slurry, the components are mixed for preferably 10 minutes or more, more preferably 30 minutes or more.



## &lt;Step (b)&gt;

[0052] In Step (b), the slurry prepared in Step (a) is spray-dried. As a spray-drying tower, a countercurrent tower is more preferable because the thermal efficiency and the particle strength of the base particles are improved. As an atomization device for the slurry, a pressure spray nozzle is especially preferable in order to obtain a desired average particle size.

[0053] The temperature of the gas exhausted from a drying tower is preferably from 70° to 130°C, more preferably from 80° to 120°C, from the viewpoint of the thermal efficiency of the drying tower. The air blow temperature is appropriately set so that the temperature of the gas exhausted is within the above range.

[0054] An inhibitor for forming a coating film is formulated in the slurry, and the resulting slurry is spray-dried, whereby the inhibitor for forming a coating film is present on the surface of the resulting base particles and/or in the vicinity thereof, or the inhibitor for forming a coating film is present in the base particle as crystals.

[0055] Further, the detergent particles are prepared by carrying out Step (c) comprising supporting a surfactant in the base particles of the present invention.

## &lt;Step (c)&gt;

[0056] The amount of the surfactant supported in the base particles is preferably from 1 to 100 parts by weight, more preferably from 20 to 80 parts by weight, still more preferably from 30 to 70 parts by weight, especially preferably from 35 to 65 parts by weight, based on 100 parts by weight of the base particles, from the viewpoint of exhibiting the detergency. Here, the supporting amount of the anionic surfactant is preferably from 1 to 60 parts by weight, more preferably from 1 to 50 parts by weight, especially preferably from 3 to 40 parts by weight, based on 100 parts by weight of the base particles. The supporting amount of the nonionic surfactant is preferably from 1 to 45 parts by weight, more preferably from 1 to 35 parts by weight, and preferably from 4 to 25 parts by weight, based on 100 parts by weight of the base particles. In addition, an amphoteric surfactant or a cationic surfactant can be also used in combination therewith in accordance with its purpose. The term "supporting amount of the surfactant" as referred to herein does not include the amount of the surfactant added when a surfactant is added in the preparation of slurry in Step (a).

[0057] The nonionic surfactant has a melting point of preferably 40°C or lower, more preferably 30°C or lower, particularly preferably 25°C or lower, especially preferably 22°C or lower. Preferable nonionic surfactants are exemplified by, for instance, polyoxyalkylene alkyl(10 to 16 carbon atoms)phenyl ethers, alkyl(8 to 16 carbon atoms) polyglycosides, polyoxyalkylene sorbitan fatty acid(10 to 18 carbon atoms) esters, polyoxyalkylene glycol fatty acid(10 to 18 carbon atoms) esters, polyoxyethylene-polyoxypropylene block polymers, and polyoxyalkylene alkylol(fatty acid) (10 to 18 carbon atoms)amides. Preferable anionic surfactants include, for instance, salts of sulfuric acid esters of which alcohol moiety has 10 to 18 carbon atoms, salts of sulfuric acid esters of an alkoxylated product of which alcohol moiety has 8 to 20 carbon atoms, alkyl(10 to 18 carbon atoms)benzenesulfonates, paraffin(10 to 18 carbon atoms) sulfonates,  $\alpha$ -olefin(10 to 16 carbon atoms) sulfonates, salts of  $\alpha$ -sulfofatty acids(10 to 18 carbon atoms), salts of alkyl ester of  $\alpha$ -sulfofatty acids(10 to 18 carbon atoms) and fatty acid salts. Especially in the present invention, preferable are linear alkylbenzenesulfonates of which alkyl moiety has 10 to 14 carbon atoms, more preferably 12 to 14 carbon atoms. As the counter ions, alkali metals and amines are preferable, and especially sodium ions and/or potassium ions, monoethanolamine and diethanolamine are preferable.

[0058] A process for supporting a surfactant in the base particles includes, for instance, a process comprising mixing the base particles with a surfactant by using a mixer for a batch process or continuous process. In the case of mixing by a batch process, as a process of supplying to a mixer, there may be employed such processes as (1) a process comprising previously supplying base particles in a mixer, and thereafter adding a surfactant thereto; (2) a process comprising supplying base particles and a surfactant in the mixer in small amounts at a time; (3) a process comprising supplying a part of base particles in a mixer, and thereafter supplying the remaining base particles and a surfactant in the mixer in small amounts at a time, and the like.

[0059] Among these processes, especially in the above (1), it is preferable that the surfactant is added in a liquid state, and it is more preferable that the surfactant in a liquid state is supplied by spraying. The addition processes mentioned above are preferable, because the detergent particles can be prepared while keeping the uni-core property of the base particle.

[0060] It is preferable that the detergent particles of the present invention are uni-core detergent particles, from the viewpoint of the solubility.

[0061] As an index for expressing the uni-core property of the detergent particles obtained through Step (c), the degree of particle growth as defined by the following equation:

$$\text{Degree of Particle Growth} = \frac{\text{Average Particle Size of Final Detergent Particles}}{\text{Average Particle Size of Base Particles}}$$



can be employed. The uni-core detergent particles in the present invention have a degree of particle growth of preferably 1.5 or less, more preferably 1.3 or less.

**[0062]** Here, "final detergent particles" refer to either of the detergent particles obtained after Step (c), or the detergent particles obtained from subjecting the resulting particles to surface modification treatment.

**[0063]** The uni-core particle can be confirmed by at least one method selected from Method ( $\alpha$ ), Method ( $\beta$ ), and Method ( $\gamma$ ) described below.

Method ( $\alpha$ ): a method of confirming the uni-core property of the detergent particle comprising splitting some of the detergent particles arbitrarily sampled from the detergent particles of a size near its average particle size, and observing presence or absence of the base particle and the number of the base particle in the detergent particle by SEM observation. It is found that the detergent particle contained in the detergent particles of the present invention is a uni-core detergent particle comprising a base particle as a core.

Method ( $\beta$ ): a method comprising extracting an organic solvent-soluble component in the detergent particle with an organic solvent which does not dissolve the water-soluble polymer in the base particle in the detergent particle [for instance, in the case where a polyacrylate is present as a water-soluble polymer, and an anionic surfactant (LAS) or a nonionic surfactant is present as a surfactant in the base particle, ethanol can be favorably used.]; and thereafter observing an organic solvent-insoluble component by SEM observation. In other words, in the case where one base particle is present in the organic solvent-insoluble component obtained by treating a single detergent particle with the above organic solvent, the detergent particle is found to be a uni-core detergent particle.

Method ( $\gamma$ ): a method of confirming the uni-core property of the detergent particle comprising detecting a two-dimensional elemental distribution of the split cross section of the detergent particle embedded in the resin by means of EDS or EPMA.

**[0064]** Among the surfactants, those which are present as solid or pasty states even if heated to, for instance, from 50° to 90°C, are previously dispersed or dissolved in a nonionic surfactant having low viscosity, an aqueous solution of a nonionic surfactant, or water, to prepare a liquid mixture or aqueous solution of a surfactant, to be added to the base particles in the form of a liquid mixture or aqueous solution. By this process, those surfactants which are present in solid or pasty form can be easily added to the base particles, thereby making it further advantageous in the preparation of the uni-core detergent particles. The mixing ratio of the surfactant having a low viscosity or water to the solid or pasty surfactant is preferably such that the resulting liquid mixture or aqueous solution has a viscosity range of which is sprayable.

**[0065]** The process for preparing the above liquid mixture includes, for instance; a process for mixing by supplying a solid or pasty surfactant to a surfactant having a low viscosity or water; or a process for preparing a surfactant mixture by neutralizing an acid precursor of a surfactant, for instance, an acid precursor of an anionic surfactant, with an alkalinizing agent, for instance, an aqueous sodium hydroxide or an aqueous potassium hydroxide, in a surfactant having a low viscosity or water.

**[0066]** Also, in this Step, an acid precursor of an anionic surfactant can be also added before adding a surfactant, simultaneously with adding a surfactant, in the course of adding a surfactant, or after adding a surfactant. By adding the acid precursor of an anionic surfactant, there can be achieved improvements in properties and quality, such as high concentration of the surfactants, control for the oil-absorbing ability of the base particles, and suppression of bleed-out of the nonionic surfactant and the flowability of the detergent particles.

**[0067]** The acid precursor of an anionic surfactant which can be used in the present invention includes, for instance, alkylbenzenesulfonic acids, alkyl ether or alkenyl ether sulfuric acids, alkyl- or alkenylsulfuric acids,  $\alpha$ -olefinsulfonic acids,  $\alpha$ -sulfonated fatty acids, alkyl ether or alkenyl ether carboxylic acids, fatty acids, and the like. It is especially preferable that the fatty acid is added after adding the surfactant, from the viewpoint of improvement in the flowability of the detergent particles.

**[0068]** The amount of the acid precursor of an anionic surfactant used is preferably from 0.5 to 30 parts by weight, more preferably from 1 to 20 parts by weight, still more preferably from 1 to 10 parts by weight, especially preferably from 1 to 5 parts by weight, based on 100 parts by weight of the base particles. Here, the amount of the acid precursor used is not counted as the amount of the surfactant in the present invention. The amount of the acid precursor of an anionic surfactant used in this range has a tendency of maintaining uni-core property of the particle in the detergent particles, and thus excellent fast dissolubility is exhibited. In addition, as the process for adding the acid precursor of an anionic surfactant, it is preferable that those in a liquid state at a normal temperature are supplied by spraying, and that those in a solid state at a normal temperature may be added as a powder, or they may be supplied by spraying after melting the solid. Here, in a case of adding the acid precursor as a powder, it is preferable that the temperature of the detergent particles in the mixer is raised to a temperature at which the powder melts.

**[0069]** As mixers preferably usable for Step (c), from the viewpoint of preparing detergent particles comprising a uni-core detergent particle in a large amount, are those mixers less likely to apply strong shearing force to the base particle

(i.e. those mixers less likely to cause disintegration of the base particle), and from the viewpoint of the dispersion efficiency of the surfactants, are those mixers with good mixing efficiency. A particular preference is given to a mixer comprising an agitating shaft arranged along the center line of a horizontal, cylindrical blending vessel and agitating impellers arranged on the agitating shaft, to carry out blending of the powders (horizontal mixers), including Lödige Mixer, PLOUGH SHARE Mixer, and the like. In addition, those mixers listed above in a continuous process can be also used to support the surfactant in the base particles. Also, as the mixers for a continuous process other than those listed above, there can be used, for instance, Flexo Mix (manufactured by Powrex Corp.); TURBULIZER (manufactured by Hosokawa Micron Corp.), and the like.

**[0070]** In addition, in this Step, when a nonionic surfactant is used, it is preferable that a water-soluble, nonionic organic compound having a melting point of 45° to 100°C and a molecular weight of 1000 to 30000 and having a function of elevating the melting point of the nonionic surfactant (hereinafter referred to as "melting point-elevating agent"), or an aqueous solution thereof, is added before adding a surfactant, simultaneously with adding a surfactant, in the course of adding a surfactant, or after adding a surfactant, or previously mixed with a surfactant. By adding the melting point-elevating agent, the caking property of the detergent particles and the bleed-out property of the surfactants in the detergent particles can be suppressed. The melting point-elevating agent which can be used in the present invention includes, for instance, polyethylene glycols, polypropylene glycols, polyoxyethylene alkyl ethers, pluronic type nonionic surfactants, and the like.

**[0071]** The amount of the melting point-elevating agent used is preferably from 0.5 to 8 parts by weight, more preferably from 0.5 to 5 parts by weight, most preferably from 1 to 3 parts by weight, based on 100 parts by weight of the base particles. The above range is preferable from the viewpoints of the suppression of aggregation between particles, the fast dissolubility, and the suppression of the bleed-out property and the caking property, each property of which is owned by the detergent particle contained in the detergent particles. As a process for adding the melting point-elevating agent, addition of a mixture prepared by previously mixing the melting point-elevating agent with a surfactant by an arbitrary process, or addition of a surfactant, followed by the addition of the melting point-elevating agent, is advantageous for the suppression of the bleed-out property and the caking property of the detergent particles.

**[0072]** As to the temperature within the mixer in this Step, it is more preferable that mixing is carried out by heating to a temperature equal to or higher than the pour point of the surfactant. Incidentally, the pour point of the surfactant is measured according to the method of JIS K 2269. Here, the temperature to be heated is preferably a temperature higher than the pour point of the surfactant added in order to promote the support of the surfactant, and the practical temperature range is preferably from a temperature exceeding a pour point to a temperature higher than the pour point by 50°C, more preferably a temperature higher than the pour point by 10° to 30°C. In addition, in the case where an acid precursor of an anionic surfactant is added in this Step, it is more preferable to mix the components after heating to a temperature at which the acid precursor of an anionic surfactant can react.

**[0073]** The mixing time in a batch process and the average residence time in the mixing in a continuous process for obtaining the suitable detergent particles are preferably from 1 to 20 minutes, more preferably from 2 to 10 minutes.

**[0074]** In addition, in the case where an aqueous solution of a surfactant or an aqueous solution of a water-soluble, nonionic organic compound is added, a step of drying excess water contents during mixing and/or after mixing may be included.

**[0075]** A powdery surfactant and/or a powdery builder can be added before adding a surfactant, simultaneously with adding a surfactant, in the course of adding a surfactant, or after adding a surfactant. By adding the powdery builder, the particle size of the detergent particles can be controlled, and an improvement in detergency can be achieved. Especially in the case where the acid precursor of an anionic surfactant is added, it is effective to add a powdery builder showing alkaline property prior to adding the acid precursor from the viewpoint of accelerating the neutralization reaction. Incidentally, the term "powdery builder" as referred to herein means an agent for enhancing detergency other than surfactants which is in a powdery form, concretely, including base materials showing metal ion capturing ability, such as zeolite and citrates; base materials showing alkalizing ability, such as sodium carbonate and potassium carbonate; base materials having both metal ion capturing ability and alkalizing ability, such as crystalline silicates; other base materials enhancing ionic strength, such as sodium sulfate; and the like.

**[0076]** Here, crystalline silicates described in Japanese Patent Laid-Open No. Hei 5-279013, column 3, line 17 (especially, those prepared by a process comprising calcinating and crystallizing at a temperature of 500° to 1000°C being preferable); Japanese Patent Laid-Open No. Hei 7-89712, column 2, line 45; and Japanese Patent Laid-Open No. Sho 60-227895, page 2, lower right column, line 18 (especially the silicates in Table 2 being preferable) can be preferably used as powdery builders. Here, the alkali metal silicates having an  $\text{SiO}_2/\text{M}_2\text{O}$  ratio, wherein M is an alkali metal, of 0.5 to 3.2, preferably from 1.5 to 2.6, are more favorably used.

**[0077]** The amount of the powdery builder used is preferably from 0.5 to 12 parts by weight, more preferably from 1 to 6 parts by weight, based on 100 parts by weight of the base particles. When the amount of the powdery builder used for a detergent is in the above range, the uni-core property of the detergent particle contained in the detergent particles is maintained, an excellent fast dissolubility is obtained, and the control for the particle size is favorable.

**[0078]** Further, it is preferable to add a step for surface-modifying the detergent particles subsequent to Step (c).

<Surface-Modifying Step>

**[0079]** In the present invention, in order to modify the particle surface of the detergent particles to which the surfactant is supported according to Step (c), there may be carried out a surface-modifying step comprising adding various surface coating agents in the form of (1) a fine powder, or (2) liquid materials in one step, or repeated in two steps.

**[0080]** Since there are tendencies of improvements in the flowability and the non-caking properties of the detergent particles when the particle surface of the detergent particles of the present invention is covered, it is preferable to include the surface-modifying step. The mixers used in the surface-modifying step are, for instance, preferably those mixers exemplified in Step (c). Each of the surface coating agents will be explained below.

(1) Fine Powder

**[0081]** As the fine powder, it is preferable that the average particle size of the primary particle is 10  $\mu\text{m}$  or less, more preferably from 0.1 to 10  $\mu\text{m}$ . The average particle size in the above range is favorable from the viewpoints of the improvements in the coating ratio of the particle surface of the detergent particles, the flowability and the anti-caking property of the detergent particles. The average particle size of the fine powder can be measured by a method utilizing light scattering by, for instance, a particle analyzer (manufactured by Horiba, LTD.), or it may be measured by a microscopic observation or the like. In addition, it is preferable that the fine powder has a high ion exchange capacity or a high alkalizing ability from the aspect of detergency.

**[0082]** The fine powder is desirably aluminosilicates which may be crystalline or amorphous. Besides the aluminosilicates, a fine powder such as sodium sulfate, sodium tripolyphosphate, calcium silicate, silicon dioxide, bentonite, talc, clay, amorphous silica derivatives, silicate compounds such as crystalline silicate compounds, is preferable. In addition, there can be also similarly used a metal soap of which primary particles have a size of 0.1 to 10  $\mu\text{m}$ , a powdery surfactant (for instance, alkylsulfates, and the like), or a water-soluble organic salt. In addition, when the crystalline silicate compound is used, it is preferably used in admixture with fine powder other than the crystalline silicate compound, for the purpose of preventing deterioration owing to aggregation of the crystalline silicates by moisture absorption and carbon dioxide absorption, and the like.

**[0083]** The amount of the fine powder used is preferably from 0.5 to 40 parts by weight, more preferably from 1 to 30 parts by weight, especially preferably from 2 to 20 parts by weight, based on 100 parts by weight of the detergent particles. When the amount of the fine powder used is in the above range, the flowability is improved, thereby giving a good texture to consumers.

(2) Liquid Materials

**[0084]** The liquid materials include aqueous solutions or molten products of water-soluble polymers, fatty acids, and the like.

(2-1) Water-Soluble Polymer

**[0085]** The water-soluble polymer includes carboxymethyl cellulose, polyethylene glycols, polycarboxylates such as sodium polyacrylates and copolymers of acryl acid and maleic acid and salts thereof, and the like. The amount of the water-soluble polymer used is preferably from 0.5 to 10 parts by weight, more preferably from 1 to 8 parts by weight, especially preferably from 2 to 6 parts by weight, based on 100 parts by weight of the detergent particles. When the amount of the water-soluble polymer used is in the above range, a powder exhibiting excellent flowability and anti-caking properties can be obtained, while the uni-core property of the detergent particle contained in the detergent particles is maintained and an excellent fast dissolubility is obtained.

(2-2) Fatty Acid

**[0086]** The fatty acid includes, for example, fatty acids having 10 to 22 carbon atoms, and the like. The amount of the fatty acid used is preferably from 0.5 to 5 parts by weight, especially preferably from 0.5 to 3 parts by weight, based on 100 parts by weight of the detergent particles. In a case of a fatty acid in a solid state at a normal temperature, it is preferable that the fatty acid is heated to a temperature showing flowability, and then supplied to the detergent particles by spraying.

**[0087]** The base particles of the present invention can be favorably utilized as a raw material for high-bulk density detergent compositions. When the detergent composition is prepared, the detergent composition may be subjected to

a treatment of densification and granulation, with adding a surfactant, as occasion demands, to the base particles obtained in Step (b) without carrying out Step (c). The applications of the base particles of the present invention are not limited particularly to a particle for supporting a surfactant as in Step (c).

**[0088]** In the present specification, the bulk density, the average particle size, the oil-absorbing ability, the water content, and the powder method of X-ray diffraction are determined as follows.

(Bulk Density): Measured by a method according to JIS K 3362.

(Average Particle Size): Measured using sieves according to JIS Z 8801. For example, nine-step sieves each having a sieve-opening of 2000  $\mu\text{m}$ , 1400  $\mu\text{m}$ , 1000  $\mu\text{m}$ , 710  $\mu\text{m}$ , 500  $\mu\text{m}$ , 355  $\mu\text{m}$ , 250  $\mu\text{m}$ , 180  $\mu\text{m}$ , or 125  $\mu\text{m}$ , and a receiving tray are used, and the sieves and the receiving tray are attached to a rotating and tapping shaker machine (manufactured by HEIKO SEISAKUSHO, tapping: 156 times/min, rolling: 290 times/min). A 100 g sample is vibrated for 10 minutes to be classified. Thereafter, the mass base frequency is sequentially cumulated for each of sieve-on granules in the order of the receiving tray, and sieves having a sieve-opening of 125  $\mu\text{m}$ , 180  $\mu\text{m}$ , 250  $\mu\text{m}$ , 355  $\mu\text{m}$ , 500  $\mu\text{m}$ , 710  $\mu\text{m}$ , 1000  $\mu\text{m}$ , 1400  $\mu\text{m}$ , and 2000  $\mu\text{m}$ . When a sieve-opening of a first sieve of which cumulative mass base frequency is 50% or more is defined as  $a \mu\text{m}$ , and a sieve-opening of one sieve-opening larger than a  $\mu\text{m}$  is defined as  $b \mu\text{m}$ , in the case where the cumulative mass base frequency from the receiving tray to the  $a \mu\text{m}$ -sieve is defined as  $c\%$ , and the mass base frequency of granules on the  $a \mu\text{m}$ -sieve is defined as  $d\%$ , the average particle size can be calculated according to the following equation:

$$(\text{Average particle size}) = 10^A:$$

wherein

$$A = \frac{50 - (c - \frac{d}{\log b - \log a} \times \log b)}{\frac{d}{\log b - \log a}}$$

**[0089]** Incidentally, the sieves used are appropriately adjusted so that the particle size distribution of powder to be measured can be accurately estimated.

(Oil-Absorbing Ability: Nonionic Surfactant Dropping Method): A cylindrical mixing vessel of an inner diameter of 5 cm and a height of 15 cm which is equipped with agitation impellers in the inner portion thereof is charged with 100 g of a sample. With stirring the contents at 350 rpm, a polyoxyethylene alkyl ether (C12/C14 = 6/4, EO = 7.7, melting point: 25°C) is supplied at a rate of 10 g/min at 30°C. The amount of polyoxyethylene alkyl ether supplied when the agitation torque reaches the highest level is defined as the oil-absorbing ability.

(Water Content: Infrared Ray Moisture Balance Method): The measurement for water content of the base particles (detergent particles) is carried out by an infrared ray moisture balance method. Specifically, 3 g of a sample is weighed on a sample plate of a known mass to the order of 0.01 g. The sample weighed is heated and dried for 3 minutes with an infrared ray moisture balance [manufactured by Ket Science Laboratory K.K. (infrared ray lamp: 185W)]. After drying, the masses of the sample plate and the dried sample are weighed to the order of 0.01 g. The difference of the masses of the plate and the sample before and after drying obtained by the above-mentioned operation was divided by the amount of the sample weighed, and the quotient is multiplied by 100 to calculate the water content in the sample.

(Powder Method of X-Ray Diffraction): Analyzed using Geiger Flex RAD-RC, Model: RU-200PL, manufactured by Rigaku Denki. The determination is made using CuK  $\alpha$ -ray as an X-ray source under the conditions of a tube voltage of 40 kV and a tube current of 120 mA.

## EXAMPLES

**[0090]** Incidentally, the properties of the resulting base particles were evaluated by the following testing methods in Examples and Comparative Examples.

(Particle Strength): A cylindrical vessel of an inner diameter of 3 cm and a height of 8 cm is charged with 20 g of a sample, and the sample-containing vessel (manufactured by Tsutsui Rikagaku Kikai K.K., "Model TVP1" tapping-type close-packed bulk density measurement device; tapping conditions: period 36 times/minute, free fall from a height of 60 mm) is tapped for 30 times. The sample height (an initial sample height) at that time is measured. Thereafter, an entire upper surface of the sample kept in the vessel is pressed at a rate of 10 mm/min with a pressing machine to obtain a load-displacement curve. The slope of the linear portion at a displacement rate of 5% or less is multiplied by an initial sample height, and the resulting product is divided by a pressed area, to give a quotient which is defined as particle strength.

[0091] In addition, the detergent particles were evaluated by the following testing methods.

(Detergency): The measurement is carried out by the method described in Japanese Patent Laid-Open No. Hei 9-241697, column 16, lines 1 to 42.

(Caking Property): An open-top carton having dimensions of 10 cm in length, 6 cm in width, and 4 cm in height is made out of a Model No. 2 filter paper defined by JIS P 3801 (for instance, qualitative No. 2 filter paper, manufactured by Toyo Roshi K.K.). A 100 g sample is placed in this box, and an acrylic resin plate and a lead plate (or an iron plate) with a total weight of 15 g + 250 g are placed on the sample. The above box is maintained in a thermohygrostat kept at a temperature of 30°C and at humidity of 80%. After 7 days, the caking conditions are evaluated. The evaluation is conducted by calculating the permeability as explained below. The higher the permeability, the lower the caking property, giving preferable properties for the detergent particles.

(Permeability): A sample after the test is gently placed on a sieve (sieve opening: 4760  $\mu$ m, as defined by JIS Z 8801), and the weight of the powder passing through the sieve is measured. The permeability based on the sample after the test is calculated.

(Bleed-Out Property): An open-top carton having dimensions of 10 cm in length, 6 cm in width, and 4 cm in height is made out of a Model No. 2 filter paper defined by JIS P 3801 (for instance, qualitative No. 2 filter paper, manufactured by Toyo Roshi K.K.). A line with a width of 0.5 to 1.0 mm is diagonally drawn on the bottom surface of the container, which is the surface of the packed sample, using a Magic Marker (manufactured by K.K. UCHIDA YOKO, "Magic Ink M700-T1"). A 100 g sample is packed in the container, and an acrylic resin plate and a lead plate (or an iron plate) with a total weight of 15 g + 250 g are placed on the sample. The container is placed in a moisture-proof container, and allowed to stand in a thermostat kept at a temperature of 30°C. After 7 days, the bleed-out property was evaluated by visually examining the degree of blur of the Magic Marker. The evaluation criteria are as follows:

Rank 5:	Blurred width of the Magic Marker being 2 cm or more;
Rank 4:	Blurred width of the Magic Marker being 1 cm or more;
Rank 3:	Blurred width of the Magic Marker being 0.5 cm or more;
Rank 2:	Slight blur of the Magic Marker being found; and
Rank 1:	No blur of the Magic Marker being found.

#### Example 1

##### (Preparation of Base Particles)

[0092] Base Particles of Example 1 were prepared by the following procedures. The composition (% by weight) of Base Particles is as shown in Table 1.

[0093] Deionized water was added to a mixing vessel having agitation impellers. After the water temperature reached 55°C, sodium chloride as an inhibitor for forming a coating film (roast salt, manufactured by Nihon Seien Co., Ltd.) was added thereto, and the resulting mixture was agitated for 15 minutes. Further, sodium sulfate (neutral anhydrous sodium sulfate, manufactured by Shikoku Kasei K.K.), sodium sulfite (sodium sulfite, manufactured by Mitsui Toatsu K.K.), and a fluorescent dye (Tinopal CBS-X, manufactured by Ciba Specialty Chemicals) were added thereto, and the resulting mixture was agitated for 15 minutes. Sodium carbonate (DENSE ASH, manufactured by Central Glass Co., Ltd) was added thereto, and the resulting mixture was agitated for 15 minutes. Thereafter, a 40% by weight-aqueous sodium polyacrylate (weight-average molecular weight: 10000, manufactured by Kao Corporation) was added thereto. The mixture was agitated for additional 15 minutes, and thereafter a crystalline sodium aluminosilicate (TOYOBUILDER, manufactured by Tosoh Corporation) was added. The resulting mixture was stirred for 30 minutes to give a homogeneous slurry. The final temperature of this slurry was 58°C. In addition, the water content in this slurry was 48% by weight. This slurry was spray-dried to give Base Particles.

Table 1

Composition	Examples						
	1	2	3	4	5	6	7
Sodium Chloride	4.0	4.0	4.0	5.2	2.0	1.0	7.5
Sodium Bromide							
Sodium Carbonate	26.0	26.0	26.0	22.4	26.0	26.0	25.0
Sodium Sulfate	22.6	27.0	23.0	16.5	24.6	26.0	21.1
Sodium Sulfite	1.0	0.0	1.0	0.9	1.0	1.0	1.0
Crystalline Sodium Aluminosilicate	36.0	33.0	26.0	42.2	36.0	36.0	28.0
Sodium Polyacrylate	6.0	6.0	6.0	7.8	6.0	6.0	15.0
Fluorescent Dye	0.4	0.0	0.4	0.4	0.0	0.4	0.4
P-type Crystalline Sodium Aluminosilicate	0.0	0.0	10.0	0.0	0.0	0.0	0.0
Water Content	4.0	4.0	3.6	4.6	4.4	3.6	2.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Polymer/Inhibitor	1.5	1.5	1.5	1.5	3.0	6.0	2.0

- continued -

- continued -

Composition	Examples			Comparative Examples			
	8	9	10	1	2	3	4
Sodium Chloride	7.0	7.0	4.0	0.0	0.0	0.1	32.0
Sodium Bromide							
Sodium Carbonate	25.0	25.0	26.0	26.0	28.9	26.0	18.0
Sodium Sulfate	23.5	21.5	22.6	26.6	21.2	24.5	15.0
Sodium Sulfite	1.0	0.0	1.0	1.0	1.1	1.0	1.0
Crystalline Sodium Aluminosilicate	28.5	28.5	36.0	36.0	32.2	32.0	25.0
Sodium Polyacrylate	14.0	15.0	6.0	6.0	10.0	12.0	3.0
Fluorescent Dye	0.0	0.0	0.4	0.4	0.4	0.4	0.4
P-type Crystalline Sodium Aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Water Content	1.0	3.0	4.0	4.0	6.2	4.0	5.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Polymer/Inhibitor	2.0	2.1	1.5	∞	∞	120.0	0.09

(Preparation of Detergent Particles)

[0094] Under mixing at 80°C, 13 parts by weight of a polyoxyethylene alkyl ether (EMULGEN 108KM; EO = 8.5, manufactured by Kao Corporation), 1.5 parts by weight of a polyethylene glycol (K-PEG6000, weight-average molecular



weight: 8500, manufactured by Kao Corporation), palmitic acid (LUNAC P-95, manufactured by Kao Corporation) equivalent to 0.5 parts by weight of sodium palmitate, LAS acid precursor (NEOPELEX FS, manufactured by Kao Corporation) equivalent to 15 parts by weight of LAS-Na, and an aqueous sodium hydroxide as a neutralizing agent were mixed, thereby giving a mixed solution of hydrated surfactant. Next, 50 parts by weight of the above Base Particles were supplied into Lödige Mixer (manufactured by Matsuzaka Giken Co., Ltd.; capacity: 20 L; equipped with a jacket), and agitations of a main shaft (150 rpm) and a chopper (4000 rpm) were initiated. Incidentally, hot water at 80°C was allowed to flow into the jacket at 10 L/minute. The above hydrated surfactant mixture was supplied into the above mixer over a period of 2 minutes, and thereafter the components were agitated for 4 minutes. Thereafter, 8 parts by weight of a crystalline silicate (SKS-6, manufactured by Clariant-Japan K.K.), 4 parts by weight of an amorphous aluminosilicate (TOYOESTA, manufactured by Tosoh Corporation), and 8 parts by weight of a crystalline aluminosilicate (TOY-OBUILDER, manufactured by Tosoh Corporation) were added to carry out surface modification for 2 minutes. Further, 1 part by weight of a crystalline aluminosilicate and 1 part by weight of an enzyme granule were added, thereby giving detergent particles. The composition and the properties of the resulting base particles, and the results of evaluation of the detergent particles are shown in Tables 1 and 2.

Table 2

	Examples						
	1	2	3	4	5	6	7
<u>Properties of Base Particles</u>							
Water Content of Slurry [%]	48	51	48	42	49	49	52
Dissolution Ratio * [%]	100	100	100	100	100	100	100
Average Particle Size [ $\mu\text{m}$ ]	250	220	250	250	250	250	250
Bulk Density [g/L]	540	510	530	700	570	560	540
Particle Strength [ $\text{kg}/\text{cm}^2$ ]	210	130	190	370	200	250	350
Oil-Absorbing Ability [g/g]	0.46	0.46	0.49	0.33	0.35	0.29	0.40
<u>Detergent Particle</u>							
Average Particle Size [ $\mu\text{m}$ ]	300	280	320	340	330	300	300
Caking Property [%]	100	100	100	100	100	100	100
Bleed-out Property	1	1	1	1	1	1	1

- continued -

\*: Dissolution ratio of the inhibitor for forming a coating film.

- continued -

	Examples				Comparative Examples			
	8	9	10	11	1	2	3	4
<u>Properties of Base Particles</u>								
Water Content of Slurry [%]	52	52	48	-	48	40	48	48
Dissolution Ratio * [%]	100	100	100	-	-	-	100	100
Average Particle Size [ $\mu\text{m}$ ]	250	250	250	-	270	230	270	250
Bulk Density [g/L]	530	550	550	-	520	620	510	500
Particle Strength [ $\text{kg}/\text{cm}^2$ ]	320	310	200	-	300	270	300	260
Oil-Absorbing Ability [g/g]	0.41	0.38	0.41	-	0.15	0.12	0.08	0.45
<u>Detergent Particle</u>								
Average Particle Size [ $\mu\text{m}$ ]	310	310	290	-	430	370	460	300
Caking Property [%]	100	100	100	100	83	75	70	95
Bleed-out Property	1	1	1	1	2	3	3	1

Examples 2 to 10, Comparative Examples 1 to 4

[0095] Each group of Base Particles and Detergent Particles of Examples 2 to 10 and Comparative Examples 1 to 4 was prepared using similar procedures. The composition and the properties of each group of Base Particles, and the results of evaluation of each group of Detergent Particles are shown in Tables 1 and 2. The P-type crystalline aluminosilicate of Example 3 was Doucil A24 (manufactured by Crosfield), and added simultaneously with TOYOBUILDER.

(Preparation of Detergent Composition)

Example 11

[0096] One-hundred parts by weight of Detergent Particles of Example 1, 3 parts by weight of a bleaching agent, 2 parts by weight of a bleaching activator, 1 part by weight of cellulase, and 1 part by weight of protease were mixed, to give Detergent Composition of Example 11. As a bleaching agent, sodium percarbonate (manufactured by Mitsubishi Gas Chemical Company, Inc.) was used. A bleaching activator used was one described in Japanese Patent Laid-Open No. Hei 8-3593, column 18, lines 14 to 37. A cellulase used was the alkaline cellulase described in Japanese Patent Laid-Open No. Hei 6-343461, and a protease used was the alkaline protease K-16 described in Japanese Patent Laid-Open No. Hei 5-25492. These enzymes were used as an enzyme particle prepared by the following methods.

[0097] Cellulase: A slurry having a slurry water content of 55% by weight was prepared from 67 parts by weight of a crystalline aluminosilicate (TOYOBUILDER, manufactured by Tosoh Corporation), 11 parts by weight of an aqueous sodium polyacrylate (weight-average molecular weight: 20000, manufactured by Kao Corporation), 11 parts by weight of a sugar (MALTORICH MR-25, manufactured by SHOWA SANGYO CO., LTD.), 11 parts by weight of the cellulase, and water. The slurry was sprayed using a pressure spray nozzle at a spraying pressure of 2.5 MPa. A spray-drying was carried out in a countercurrent spray-drying tower (diameter: 3 m, height of the tower: 10 m) at a blowing rate of 100m<sup>3</sup>/min., a blowing temperature of 150°C and a slurry-spraying rate of 200 kg/h. Particles having a size of 1410 µm or more were removed from the resulting particle with a sieve, to give an enzyme particle having a water content value of 4.1% by weight.

[0098] Protease: A slurry having a slurry water content of 50% by weight was prepared from 57 parts by weight of a crystalline aluminosilicate (TOYOBUILDER, manufactured by Tosoh Corporation), 10 parts by weight of an aqueous sodium polyacrylate (weight-average molecular weight: 10000, manufactured by Kao Corporation), 4 parts by weight of sodium sulfate (neutral anhydrous sodium sulfate, manufactured by Shikoku Kasei K.K.), 4 parts by weight of a sugar (MALTORICH MR-25, manufactured by SHOWA SANGYO CO., LTD.), 5 parts by weight of a polyethylene glycol (K-PEG6000, weight-average molecular weight: 8500, manufactured by Kao Corporation), 20 parts by weight of the protease, and water. A spray-drying was carried out under the same conditions as the cellulase. Subsequently, particles having a size of 125 µm or less and 710 µm or more were removed with a sieve, to give an enzyme particle having a water content value of 3.8% by weight.

[0099] As is clear from the results for the oil-absorbing ability, each group of Base Particles of Examples 1 to 10, which comprises a necessary amount of sodium chloride or sodium bromide as an inhibitor for forming a coating film, has a high oil-absorbing ability as compared with those which do not contain this component. As a result, the caking property and the bleed-out property of the detergent particles are also suppressed. Incidentally, in Examples 1 to 10, the content of sodium chloride or sodium bromide is an appropriate amount, so that the detergency is not affected. In addition, in Comparative Example 3 where the amount of sodium chloride is small relative to the amount of the water-soluble polymer, the oil-absorbing ability is low, so that the effect of the addition of sodium chloride is not notably exhibited. In Comparative Example 4 where the amount of sodium chloride is extremely large relative to the amount of the water-soluble polymer, the oil-absorbing ability is high, so that the caking property and the bleed-out property are suppressed, but the detergency is remarkably lowered. In addition, with respect to Detergent Composition of Example 11, there are no problems in the caking property and the bleed-out property, and the detergency was excellent.

[0100] Each group of Base Particles in Comparative Examples 1 to 3 was analyzed by SEM observation and EDS. As a result, it was confirmed that the base particle had a coat-type particle structure in which a higher proportion of the crystalline sodium aluminosilicate was present in the inner portion of the particle, and that larger amounts of the water-soluble polymer and the water-soluble salt were present near the particle surface. In addition, in Examples 1 to 9, it was revealed that sodium chloride added was present on the particle surface. In addition, each group of Base Particles of Examples 1 to 9 and Comparative Example 4 was analyzed by powder method of X-ray diffraction. As a result, intensive peaks were detected at  $2\theta = 31.7^\circ$  and  $45.5^\circ$ , which are ascribed to the crystals of sodium chloride.

[0101] In addition, each group of the detergent particles in Examples and Comparative Examples contained uni-core detergent particles.

INDUSTRIAL APPLICABILITY

[0102] The base particles of the present invention obtainable by formulating an inhibitor for forming a coating film to a slurry, and the detergent particles have excellent dissolubility, and further have extremely high oil-absorbing ability, while having a sufficient bulk density.

[0103] The present invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

# Claims

1. Base particles for supporting a surfactant, obtainable by spray-drying a slurry comprising a water-soluble polymer (A), an inhibitor for forming a coating film (B) and a water-soluble salt (C) other than the inhibitor for forming a coating film, wherein the surfactant is contained in an amount of from 0 to 10% by weight of the base particles.
2. The base particles according to claim 1, wherein a weight ratio of the water-soluble polymer to the inhibitor for forming a coating film in a base particle constituting the base particles, i.e. water-soluble polymer/inhibitor for forming a coating film, is from 0.1 to 100.
3. The base particles according to claim 1 or 2, wherein the slurry further comprises a water-insoluble inorganic compound (D).
4. The base particles according to any one of claims 1 to 3, wherein the inhibitor for forming a coating film is an alkali metal halide.
5. The base particles according to any one of claims 1 to 4, wherein the inhibitor for forming a coating film exists on the surface of a base particle and/or its vicinity.
6. The base particles according to any one of claims 1 to 5, wherein the inhibitor for forming a coating film exists as crystals in the base particle.
7. Base particles for supporting a surfactant, obtainable by spray-drying a slurry comprising at least a water-soluble polymer (A) and an alkali metal halide, wherein the surfactant is contained in an amount of from 0 to 10% by weight of the base particles, and wherein a weight ratio of the water-soluble polymer to the alkali metal halide in a base particle constituting the base particles, i.e. water-soluble polymer/alkali metal halide, is from 0.1 to 100.
8. A process for preparing base particles for supporting a surfactant, the base particles containing the surfactant in an amount of from 0 to 10% by weight, comprising the step of spray-drying a slurry comprising a water-soluble polymer (A), an inhibitor for forming a coating film (B) and a water-soluble salt (C) other than the inhibitor for forming a coating film, wherein a dissolution ratio of Component (B) in the slurry is at a level sufficient to inhibit formation of a coating film on the surface of the resulting base particles.
9. Detergent particles having an average particle size of from 150 to 750  $\mu\text{m}$  and a bulk density of 500 g/L or more, wherein 1 to 100 parts by weight of a surfactant is supported in 100 parts by weight of the base particles of any one of claims 1 to 7.
10. The detergent particles according to claim 9, wherein the detergent particles have uni-core property.
11. A detergent composition comprising the detergent particles of claim 9 or 10.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03813

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl<sup>7</sup> C11D17/06, C11D3/37, C11D3/04, C11D11/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl<sup>7</sup> C11D17/06, C11D3/37, C11D3/04, C11D11/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, 4054541, A (Witco Chem. Corp.), 18 October, 1977 (18.10.77), Claims, Examples 1-2 (Family: none)	1-8 9-11
A	EP, 352892, A1 (Kao Corp.), 31 January, 1990 (31.01.90), & JP, 2-38497, A & US, 4999138, A & CA, 1316789, A1	1-8
A	US, 3816352, A (Witco Chem. Corp.), 11 June, 1974 (11.06.74), & DE, 2347188, A1 & FR, 2204680, A1 & CA, 973053, A1 & GB, 1412657, A	1-8
A	EP, 19470, A1 (Unilever Ltd.), 26 November, 1980 (26.11.80), & JP, 56-22394, A & US, 4298491, A & CA, 1143236, A1 & DE, 3069626, A1	1-8
A	EP, 139523, A1 (Unilever NV.), 02 May, 1985 (02.05.85), & AU, 8434432, B & JP, 60-104199, A	1-8

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
18 September, 2000 (18.09.00)Date of mailing of the international search report  
26 September, 2000 (26.09.00)Name and mailing address of the ISA/  
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03813

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	& US, 4645616, A & DE, 3481005, A1	
A	US, 5118439, A (Henkel Corp.), 02 June, 1992 (02.06.92), Claims; column 2, lines 35-36; examples & WO, 90/04630, A1	1-8
A	Database WPI on dialog, London: Derwent Publications Ltd., AN3991259, class D24, E12 SU1350171, A1 (Maslozhirprom res), abstract	1-8
A	Database WPI on dialog, London: Derwent Publications Ltd., AN831652, class D25, E34 HU34540, T (Novenyolajipari es), Abstract	1-8
P, A	JP, 11-241099, A (Kao Corp.), 07 September, 1999 (07.09.99) (Family: none)	1-8
A	JP, 11-106797, A (Kao Corp.), 20 April, 1999 (20.04.99) (Family: none)	1-8
A	EP, 76137, A1 (Unilever PLC), 06 April, 1983 (06.04.83), & AU, 8288739, B & JP, 58-67799, A & US, 4466897, A & CA, 1197159, A1 & DE, 3275204, A1	1-8
A	WO, 99/36503, A1 (Procter & Gamble Co.), 22 July, 1999 (22.07.99) (Family: none)	1-8
A	EP, 8669, A1 (Hoechst AG), 19 March, 1980 (19.03.80) & DE, 2834224, A1 & JP, 55-25478, A	1-8
A	JP, 63-199796, A (Kao Corp.), 18 August, 1988 (18.08.88) (Family: none)	1-8
A	US, 5242615, A (Henkel Corp.), 04 April, 1991 (04.04.91), claims; column 1, lines 32-35; examples & WO, 91/4313, A1	1-8
A	JP, 63-20398, A (Kao Corp.), 28 January, 1988 (28.01.88) (Family: none)	1-8
A	EP, 168102, A1 (Unilever NV.), 15 January, 1986 (15.01.86) & JP, 61-26698, A & DE, 3424987, A1 & AU, 8544538, B & US, 4639326, A & CA, 1236368, A1	1-11
A	EP, 184794, A1 (Henkel KGaA), 18 June, 1986 (18.06.86), & DE, 3444960, A1 & JP, 61-138697, A & US, 4707290, A	1-11
A	EP, 342043, A1 (Procter & Gamble Co.), 15 November, 1989 (15.11.89), & JP, 2-64199, A & US, 5009804, A & CA, 1326623, A1	1-11

Form PCT/ISA/210 (continuation of second sheet) (July 1992)



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03813

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 3-84100, A (Lion Corporation), 09 April, 1991 (09.04.91) (Family: none)	1-11
A	WO, 94/16052, A1 (Unilever PLC), 21 July, 1994 (21.07.94) & AU, 9458142, B & EP, 678119, A1 & JP, 8-505177, A	1-11
A	EP, 520582, A1 (Colgate Palmolive Co.), 30 December, 1992 (30.12.92), & AU, 9218464, B & CA, 2072506, A1 & JP, 5-247497, A	1-11
P,A	JP, 11-310791, A (Lion Corporation), 09 November, 1999 (09.11.99) (Family: none)	1-8
P,A	JP, 11-302699, A (Lion Corporation), 02 November, 1999 (02.11.99) (Family: none)	1-8
A	JP, 9-279184, A (Lion Corporation), 28 October, 1997 (28.10.97) (Family: none)	1-8
A	JP, 9-137200, A (Kao Corp.), 27 May, 1997 (27.05.97) (Family: none)	1-8
A	JP, 8-92591, A (Kao Corp.), 09 April, 1996 (09.04.96) (Family: none)	1-8
A	GB, 2156870, A (Colgate Palmolive Co.), 16 October, 1985 (16.10.85), & DE, 3509331, A1 & FR, 2562085, A1 & AU, 8540714, B & JP, 61-298, A & US, 4741851, A & US, 4857223, A & CA, 1276091, A1	1-8
A	JP, 58-213099, A (Kao Sekken K.K.), 10 December, 1983 (10.12.83) (Family: none)	1-8
A	JP, 8-231994, A (Lion Corporation), 10 September, 1996 (10.09.96) (Family: none)	1-8

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

